

Early Time Photoconductance in Quantum Dot Solids Probed by Ultrafast Photocurrent Spectroscopy

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**Center for Advanced Solar
Photophysics**

&

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Spectroscopy Team**

**Los Alamos National
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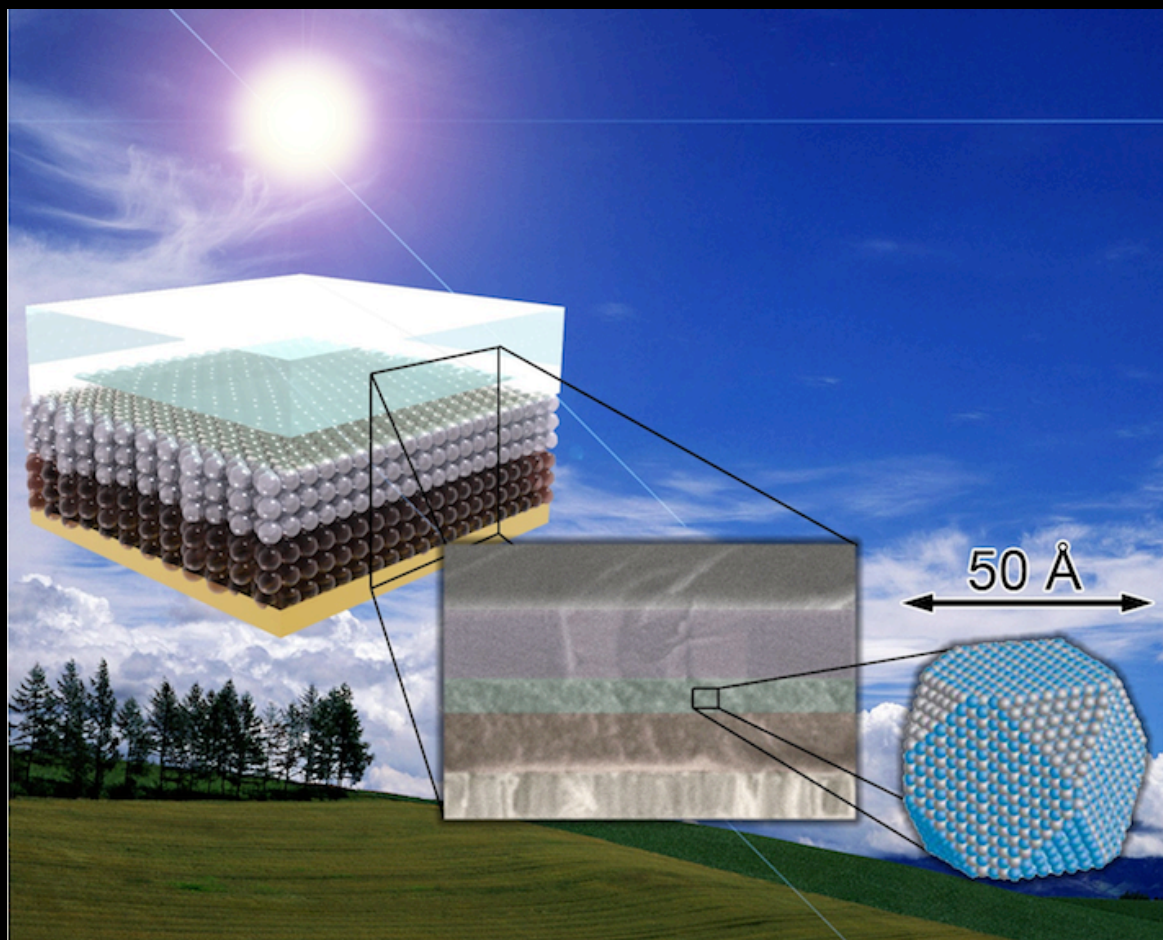
Los Alamos, NM

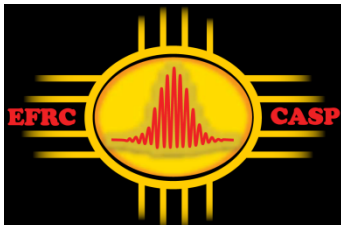
klimov@lanl.gov

<http://casp.lanl.gov>

<http://quantumdot.lanl.gov>

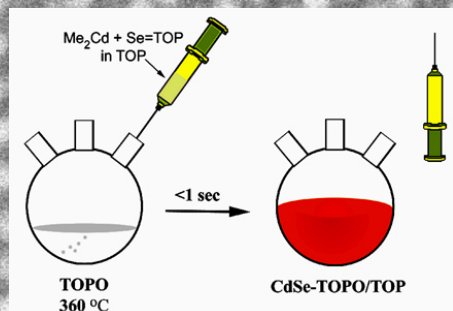
**Funding: Energy Frontier
Research Center (EFRC),
BES, Office of Science, DOE**



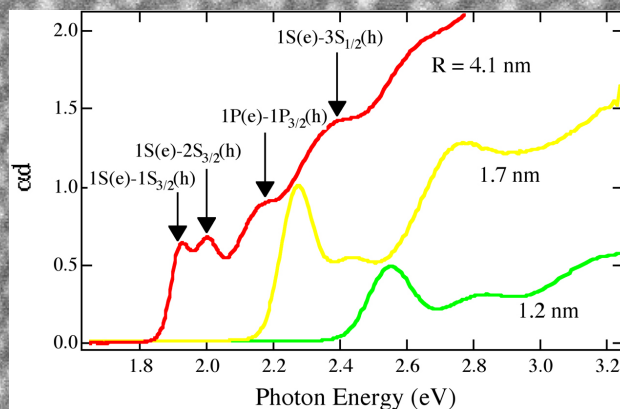


Colloidal Quantum Dots: Artificial Atoms with Tunable Properties

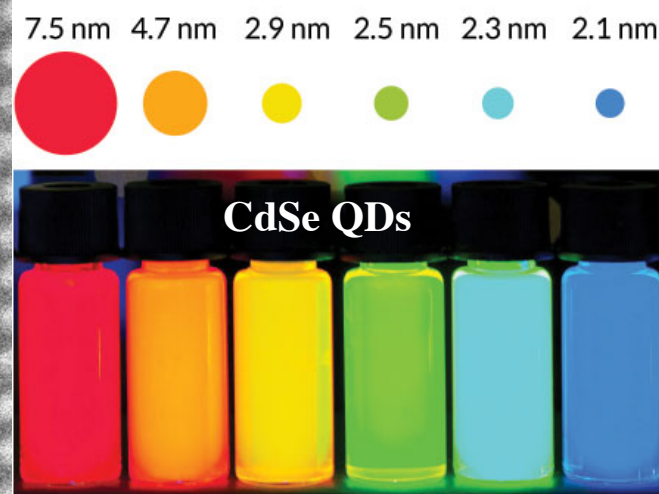
Colloidal quantum dots



$R = 10\text{--}50 \text{ \AA}$, $\Delta R/R = 4\text{--}7\%$



C. Murray, D. Norris, and M. Bawendi,
J. Am. Chem. Soc. **115**, 8706 (1993).

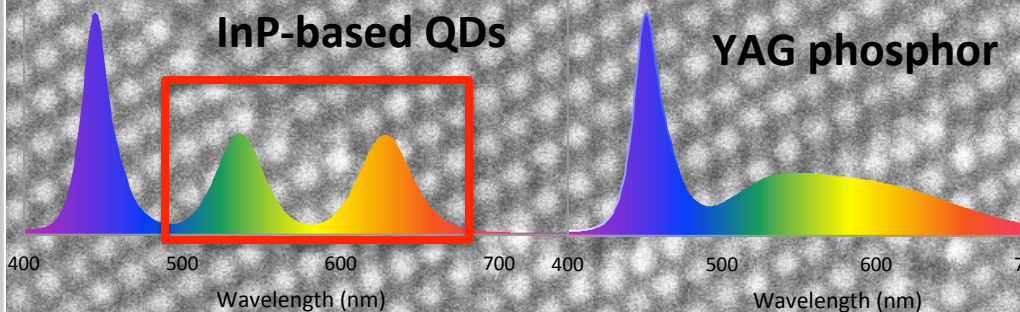


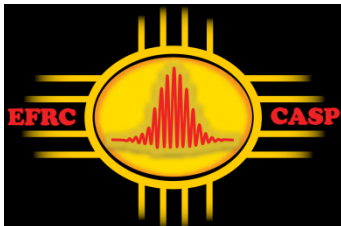
Credit: Antipoff/Wikimedia Commons

Quantum dot TVs



Samsung TV – JS9500

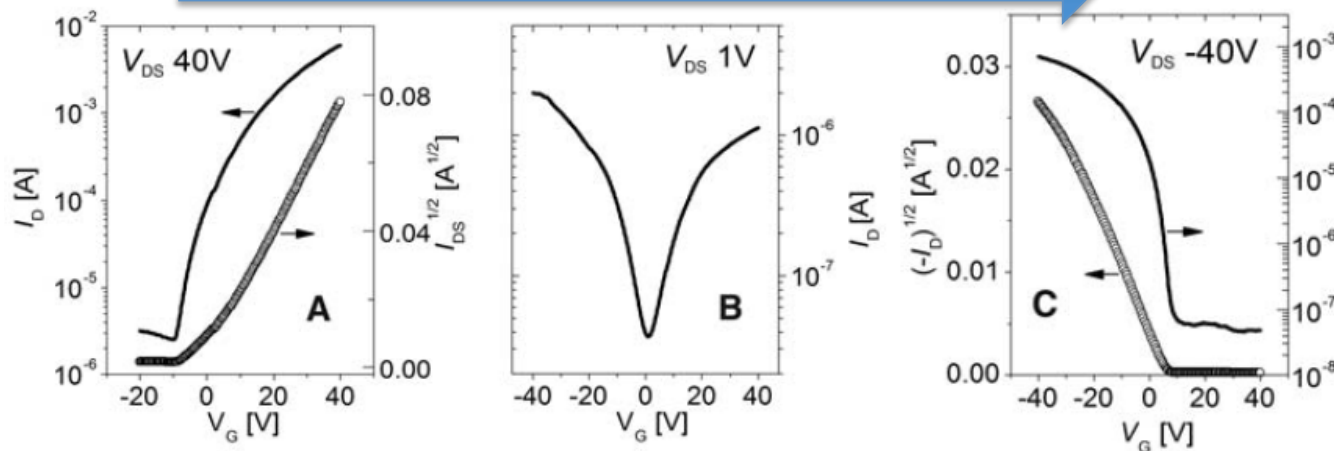




QD Doping by Ligand Exchange: “Surface Doping”

■ Charge transport (“dark”) in PbSe QD films treated with hydrazine (N_2H_4)

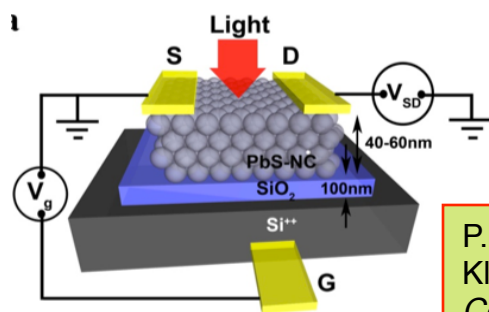
vacuum treatment or heating



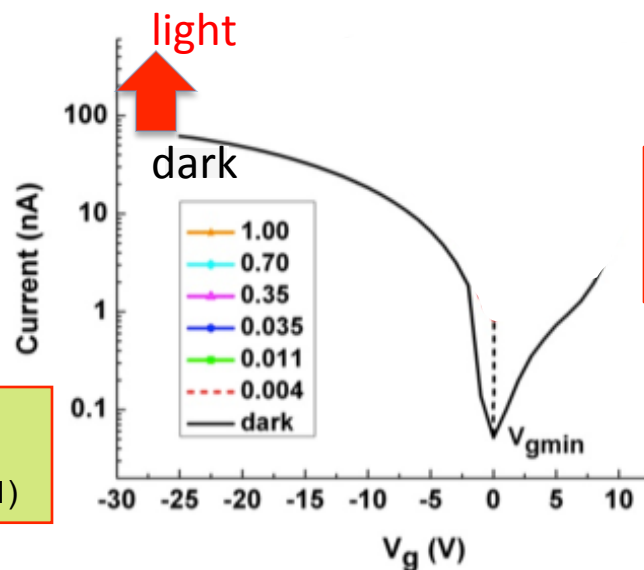
D. Talapin & C. Murray
Science **310**, 86 (2005)

Vacuum treatment or mild heating (to $\sim 100^\circ\text{C}$) of activated PbSe nanocrystal films switched their conductivity from n-type (Fig. 3A) to ambipolar (Fig. 3B) and, finally, to p-type (Fig. 3, C and D) as the hydrazine desorbed.

■ “Dark” vs. “light” transport in PbSe QD films treated with EDT [$C_2H_4(SH)_2$]

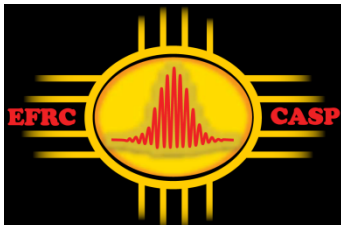


P. Nagpal & V.I. Klimov, *Nature Comm.* **2**, 486 (2011)

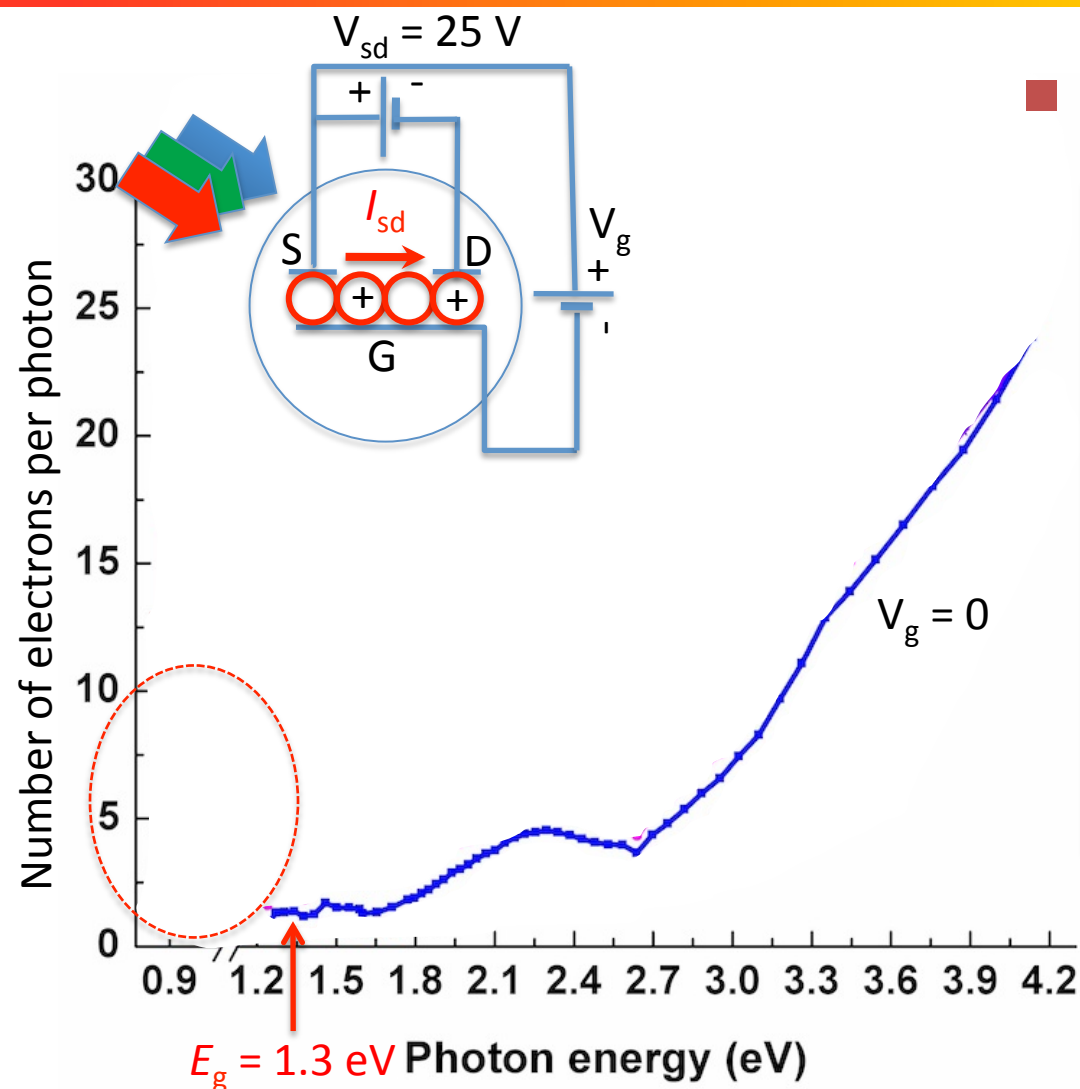


Dark: $V_g = -25 \text{ V}$; $p = 0.1/\text{QD}$
Light: $W_{\text{max}} = 50 \mu\text{W cm}^{-2}$
 $n = p < 0.0001/\text{QD}$

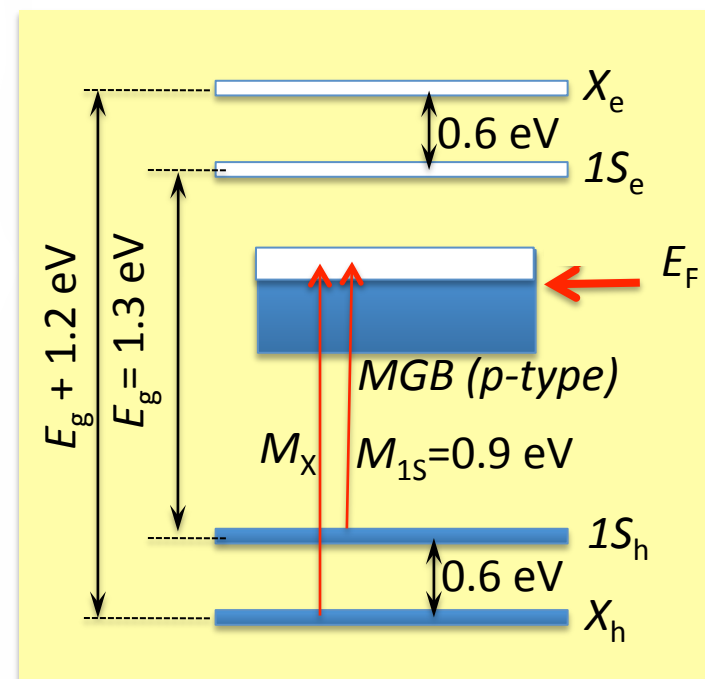
$I_{\text{sd}}(\text{light}) \gg I_{\text{sd}}(\text{dark})$
 $n(\text{light}) \ll n_0(\text{dark})$

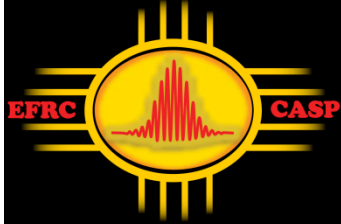


Mid-Gap States “Visualized” in Optical-FET Photocurrent Spectra



Mid-gap band (MGB)



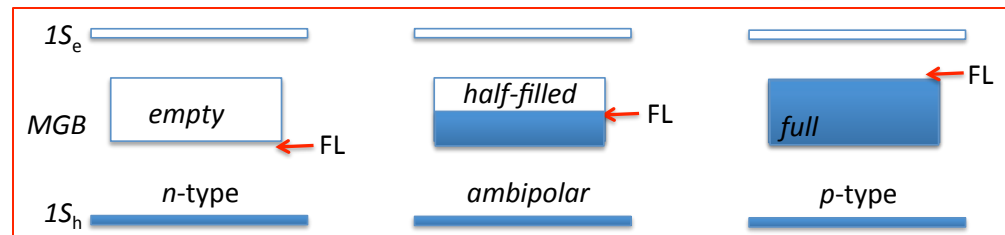
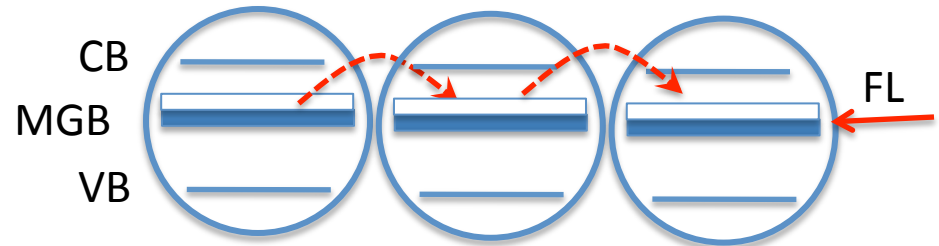


Mechanisms of Charge Transport: “Dark” vs. “Light” Conductance

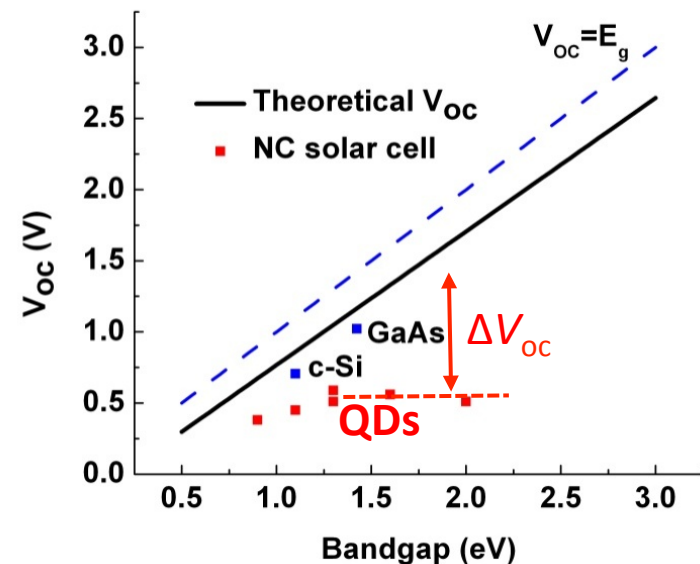
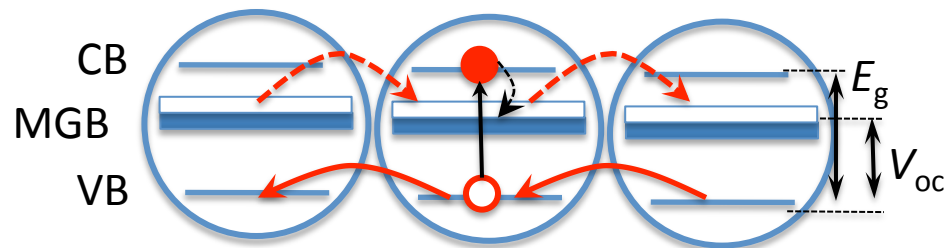
■ “Dark” conductance is due to nonintrinsic surface states forming a weakly conducting intra-gap band (MGB)

P. Nagpal & V.I. Klimov, *Nature Comm.* **2**, 486 (2011)

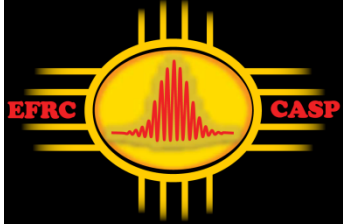
B. Pal et al., *Adv. Funct. Mat.* **22**, 1741(2012)



■ Photoconductance has “mixed” character: *photogenerated holes are transported via VB states, electrons via MGB*

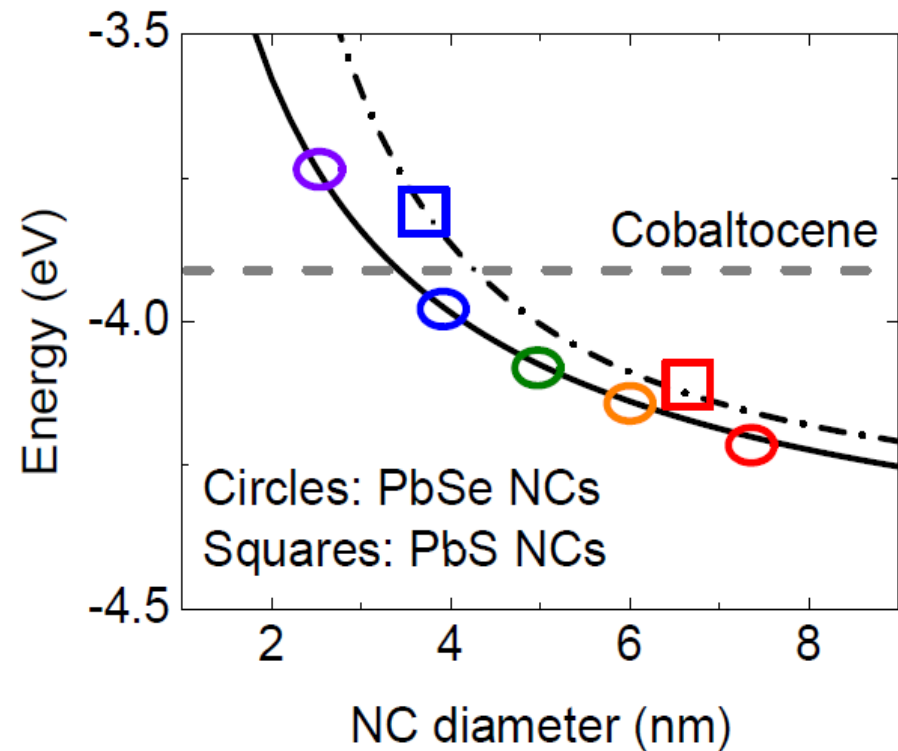
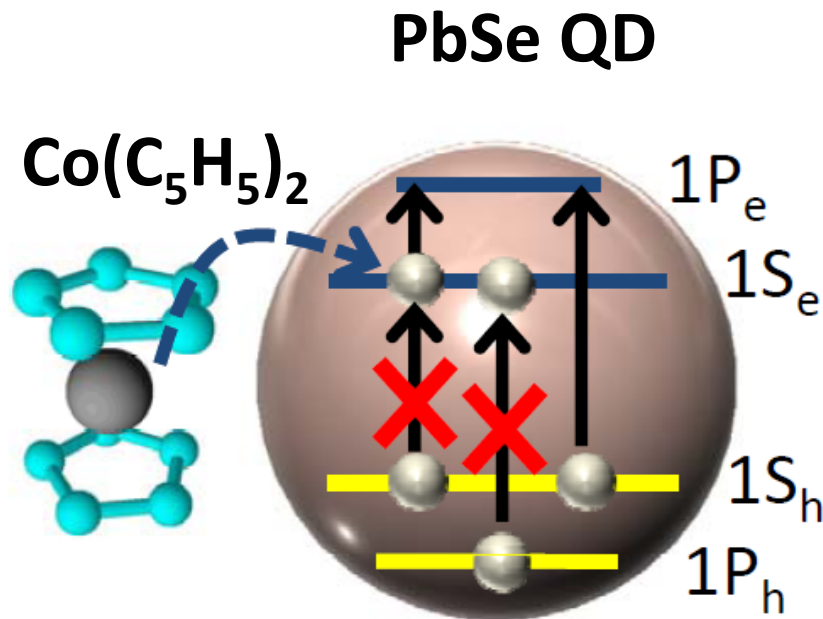


■ V_{oc} is pinned by $E_{eff} = E_g - \Delta E_{MGB-CB}$

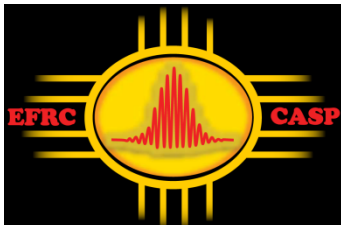


***n*-Doping of PbSe QDs by Ground-State Charge Transfer from Cobaltocene (up to 8 electrons per dot)**

■ Cobaltocene-QD electron transfer: *Energetic considerations*

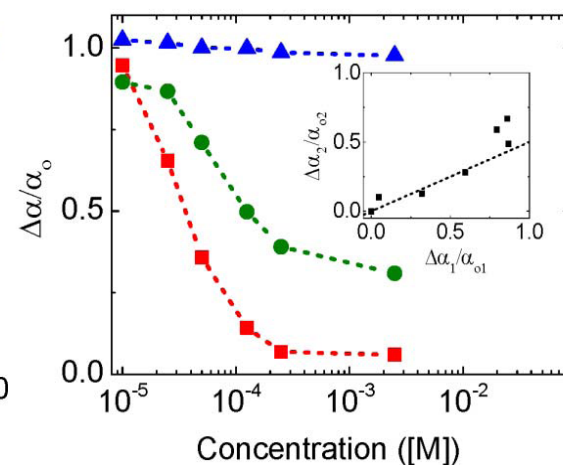
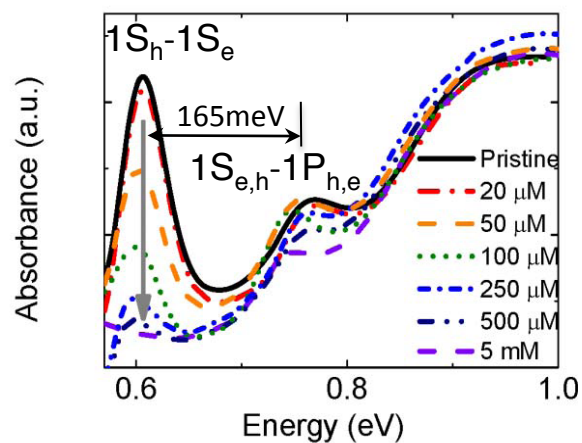
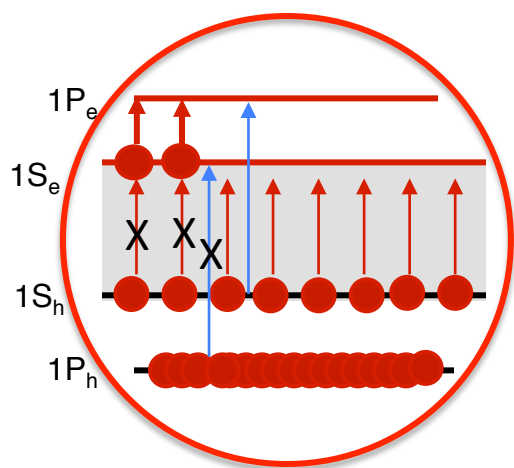


W.-k. Koh, A. Kaposov *et al.*, *Sci. Rep.* **3**, 204 (2013)

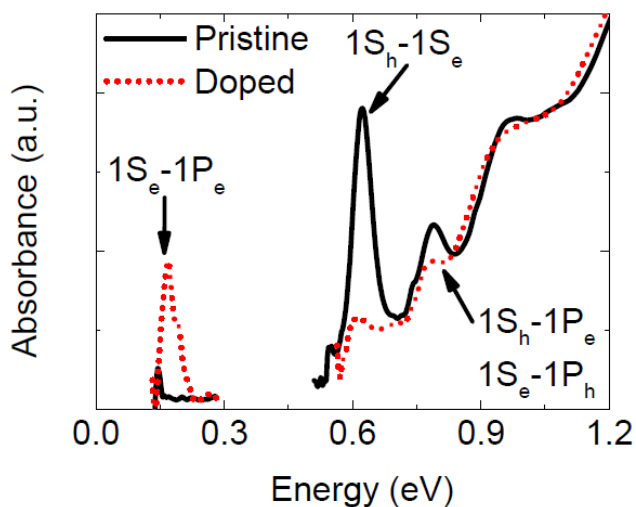


Effect of Cobaltocene-doping on Optical Spectra

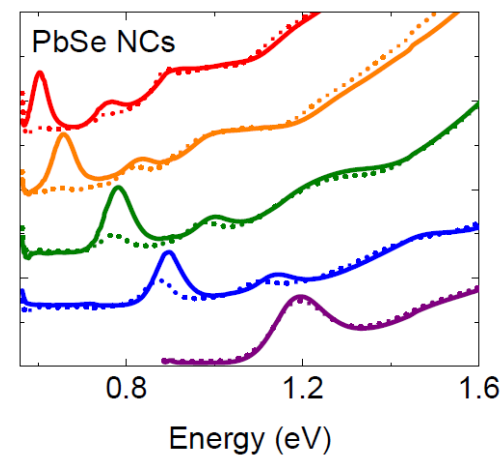
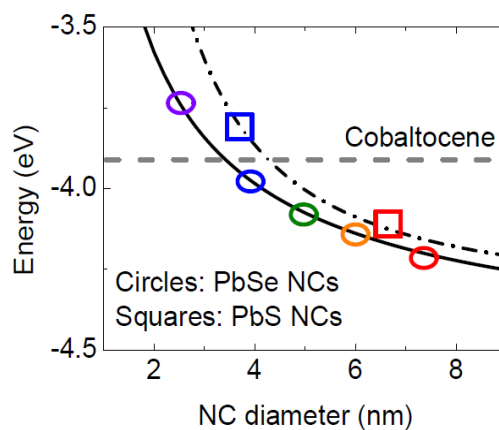
Effect on inter-band absorption

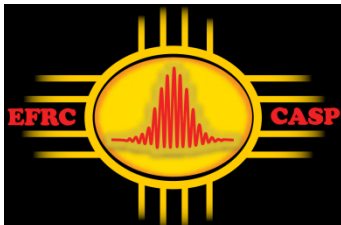


Effect on intra-band absorption



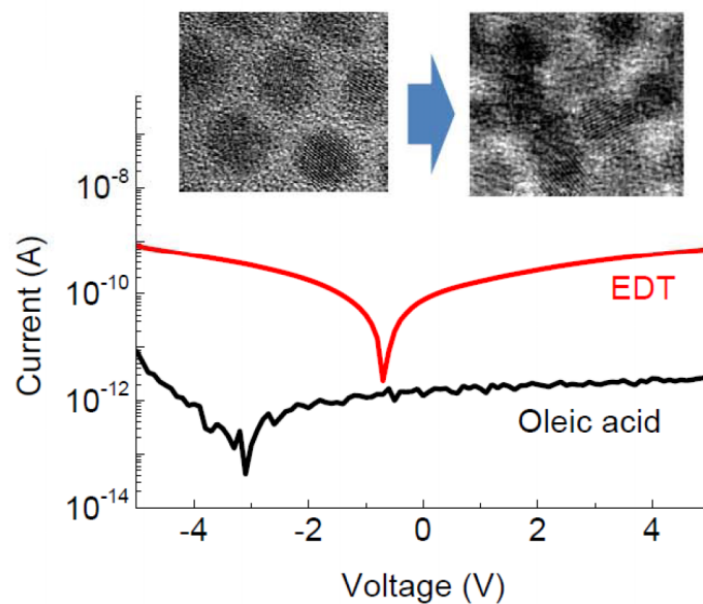
Effect on size



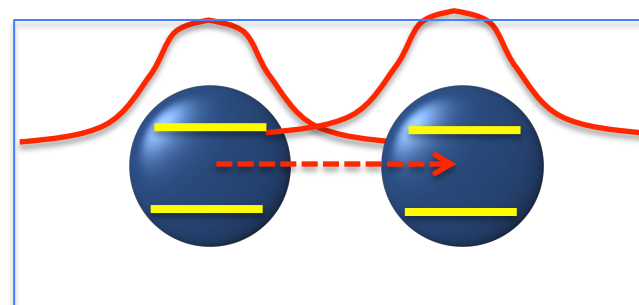
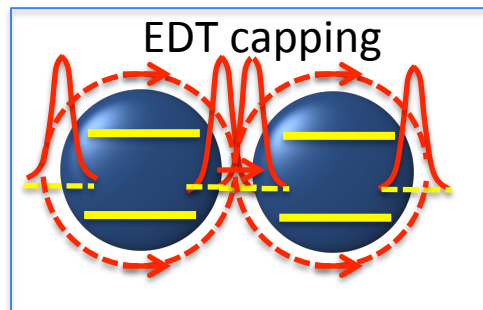
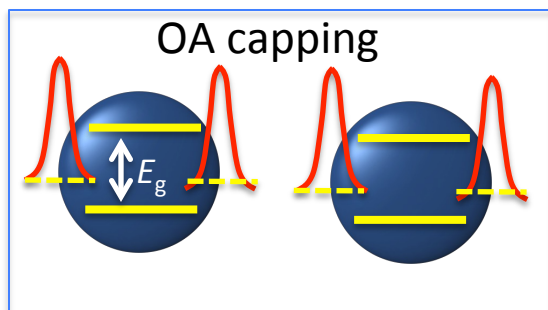
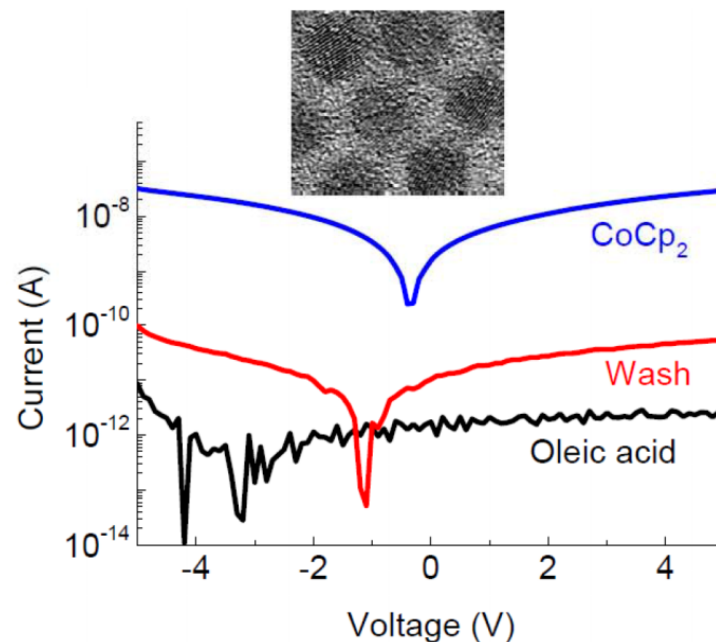


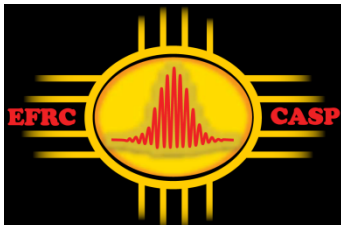
Effect of Doping on Charge Transport

■ EDT treated films: “Surface-state” transport



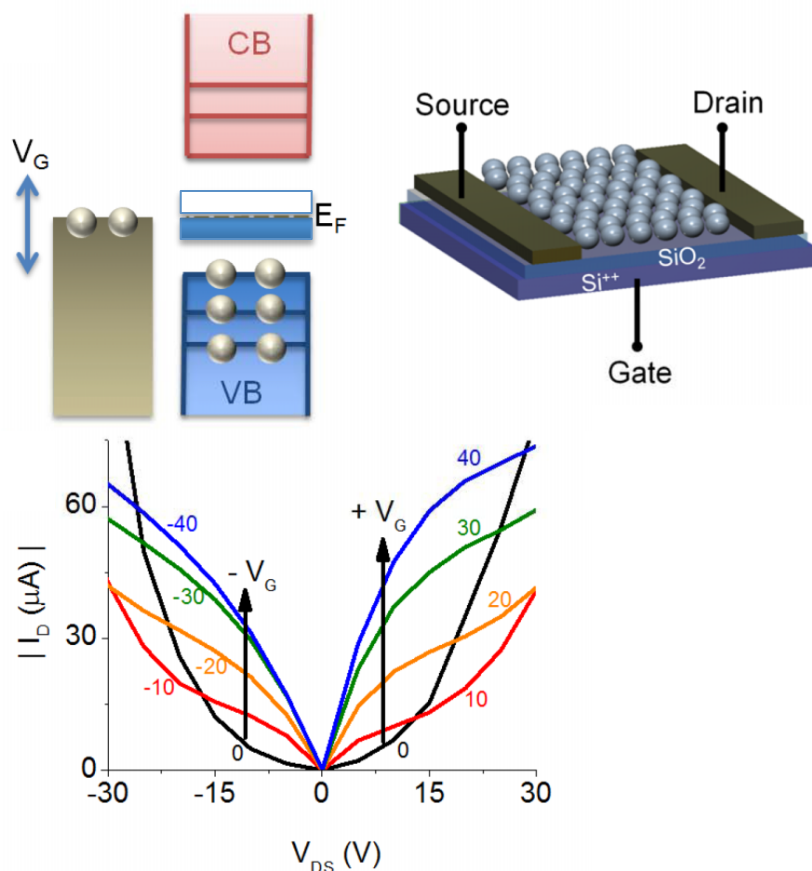
■ Cobaltocene -treated films: “Band-edge” transport via quantized states





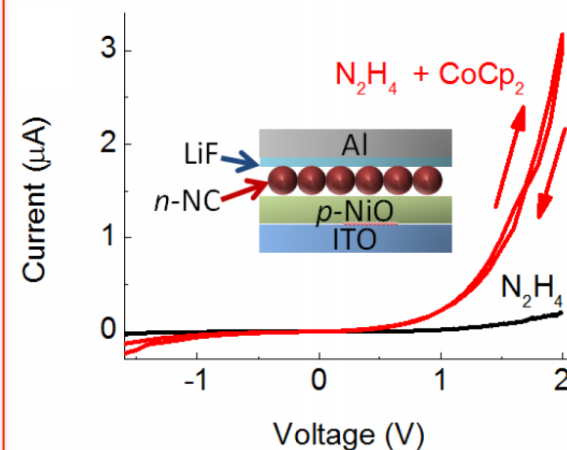
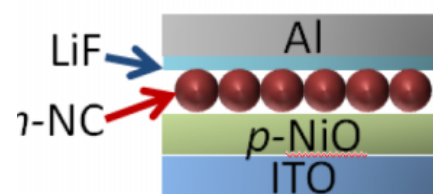
Effect of Doping Evaluated Using Field-Effect-Transistors (FETs)

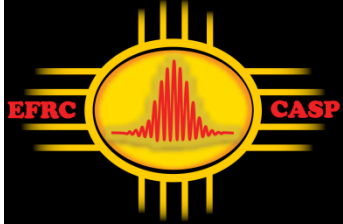
■ Undoped close-packed QDs (mild treatment with N_2H_4)



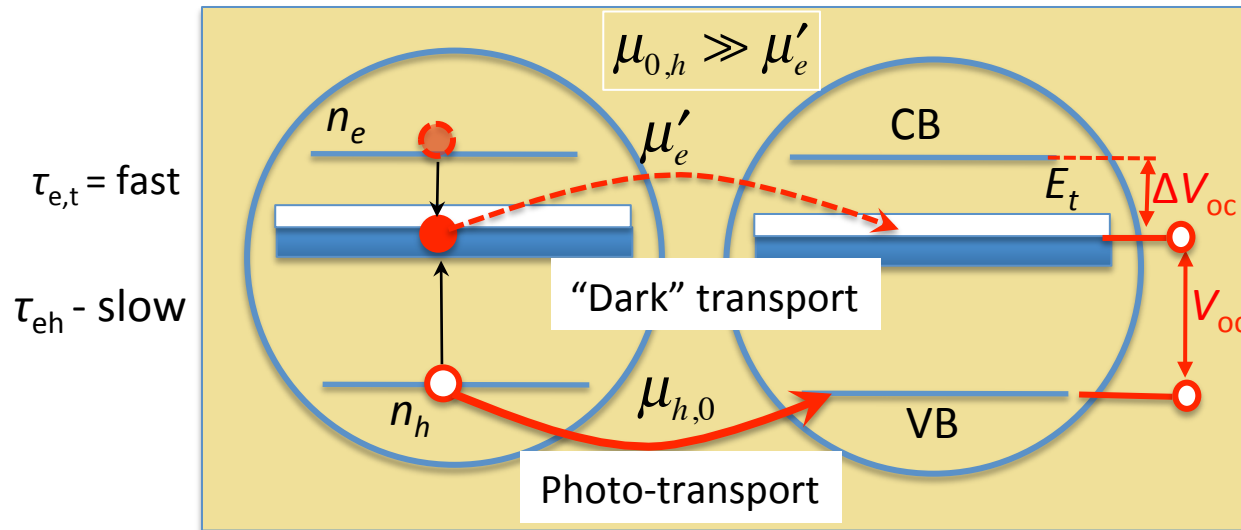
W.-k. Koh *et al.*, *Sci. Rep.* **3**, 204 (2013)

■ Rectifying $p-n$ junction using n -type QDs





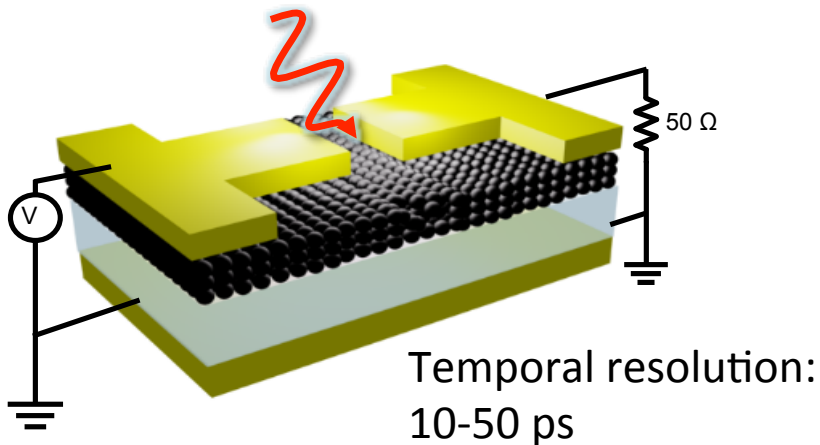
Mixed-States Photoconductance in QD solids



P. Nagpal & V.I. Klimov, *Nature Comm.* 2, (2011)

■ QD-based electro-optical Auston switch

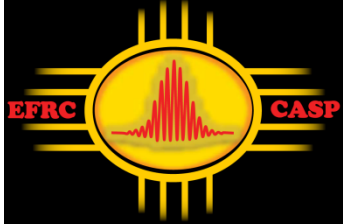
D. Auston, *IEEE J. Qu. El.* (1983)



$$j(t) = eE \sum_{l,m} \left[\mu_{n,i} n_{e,i}(t) + \mu_{p,l} p_{h,l}(t) \right]$$

Electron i -state occupancy
 Electron i -state mobility

J. Gao, A. Fidler, V. I. Klimov, *Nature Comm.* 6, 8185 (2015)
 A. Fidler, J. Gao, V.I. Klimov, *Nature Phys.* March (2017)

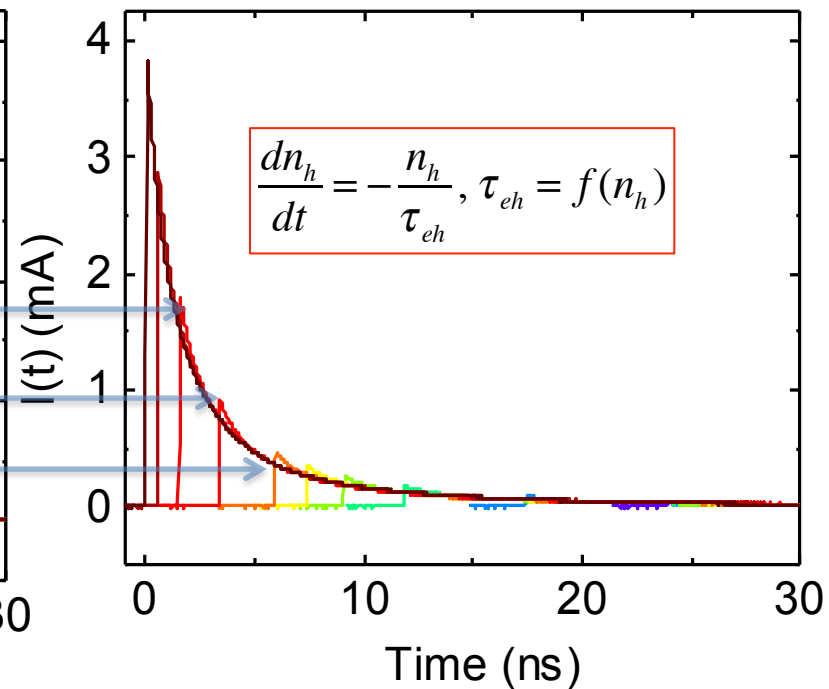
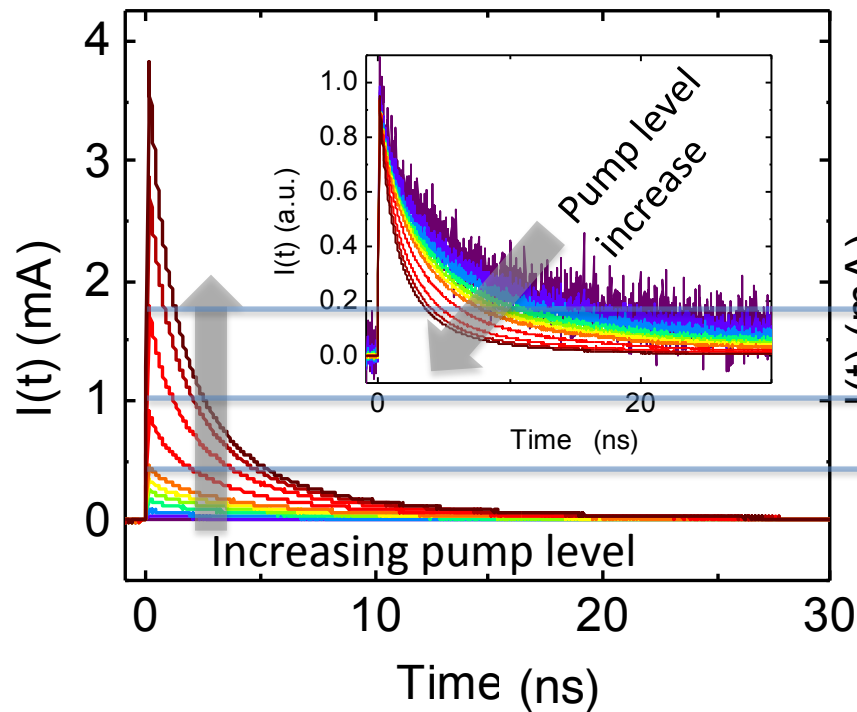


“Memory-Less” Nongeminate Recombination

■ Long-term photocurrent dynamics: 1.5 eV excitation

$E_g = 0.69$ eV; $T = 300$ K

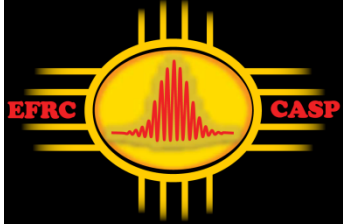
Average QD occupancy: $\langle N_0 \rangle = 0.001$ -0.15



Nonlinear nongeminate recombination

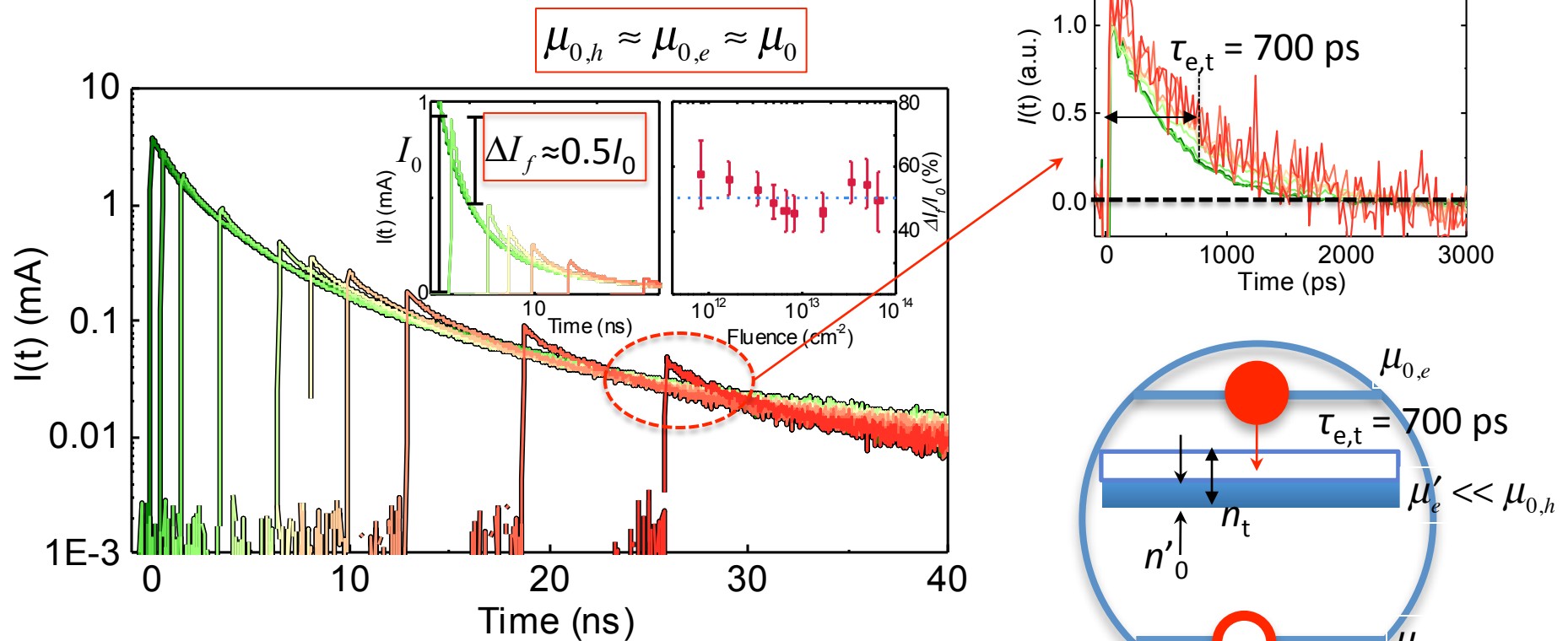
A. Fidler, J. Gao, V.I. Klimov,
Nature Phys. March, 2017

- No memory effects in recombination
- Recombination time is directly linked to concentration of mobile charges



The Origin of "Overshoot": *Electron Trapping by Deep Weakly Conducting States*

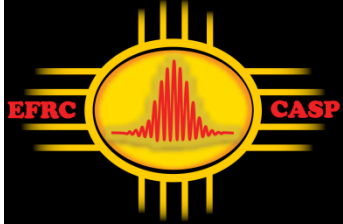
■ Electron trapping dynamics



Trapping rate proportional to concentration of pre-existing hole in the intra-gap band

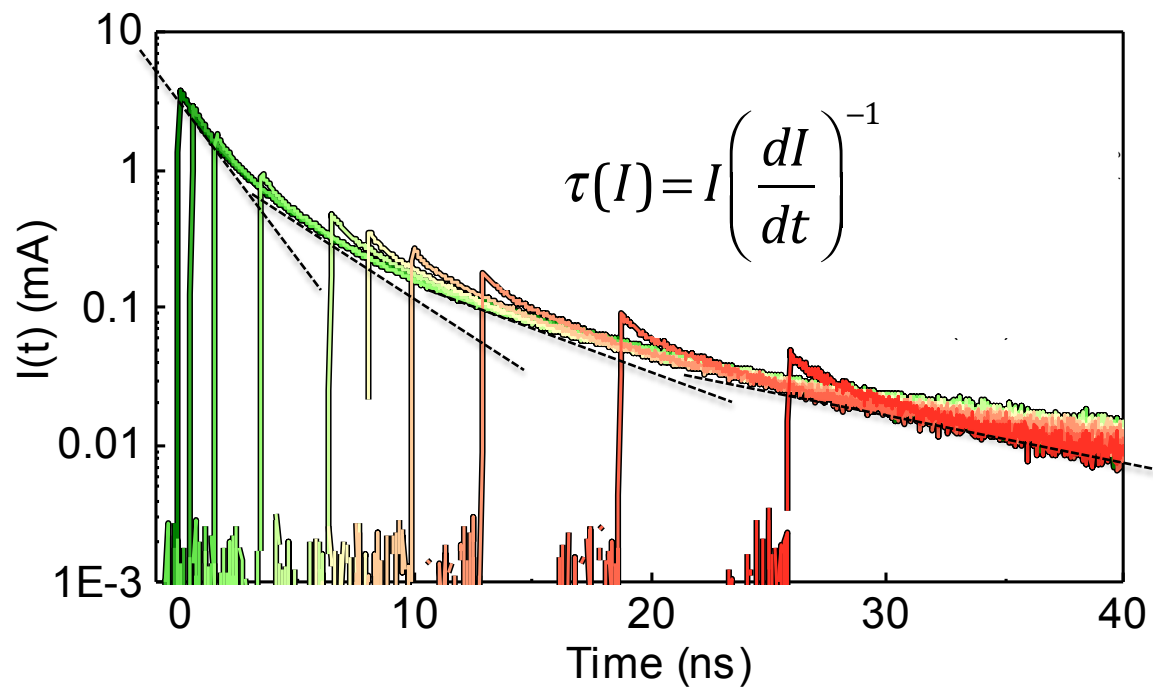
$$\frac{1}{\tau_{e,t}} = \alpha(n_t - n'_0) = (1/700) \text{ ps}^{-1}$$

A. Fidler, J. Gao, V.I. Klimov,
Nature Phys. March, 2017



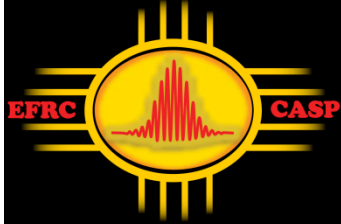
Instantaneous Relaxation Time Constant: *Unraveling the Origin of Nonexponential Decay*

■ Nonlinear, nongeminate e-h recombination



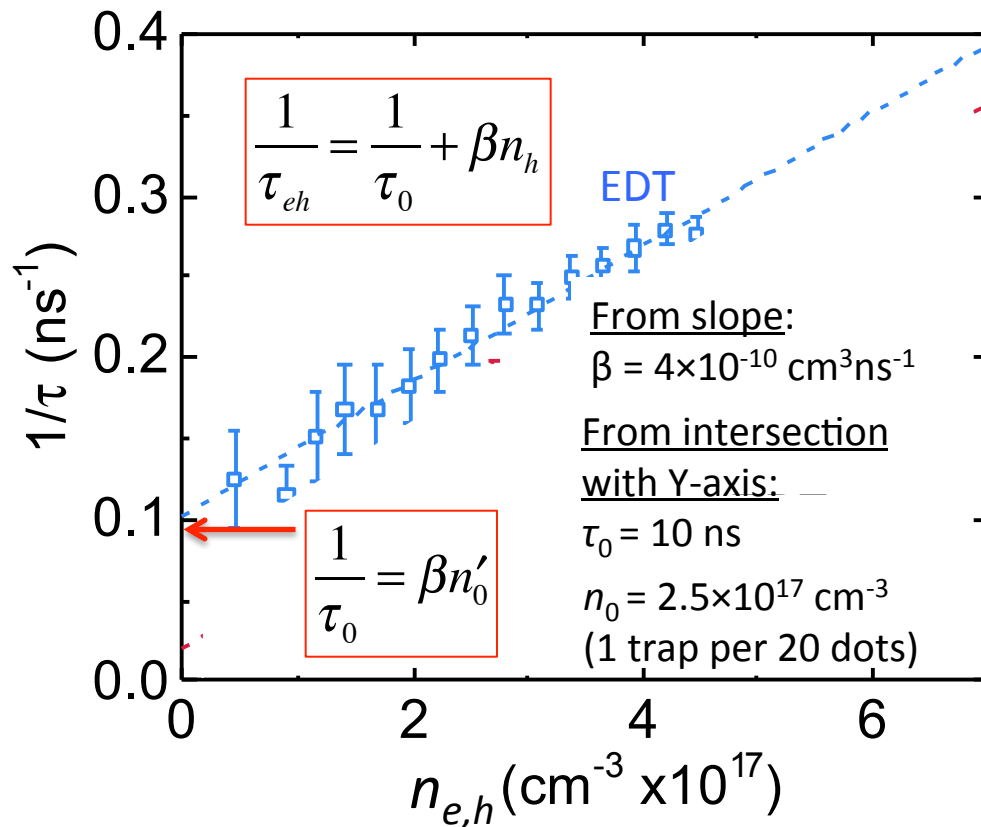
$$n_h(t) = \frac{I(t)}{e\mu_0 E}$$

$\tau \text{ vs. } n_h$



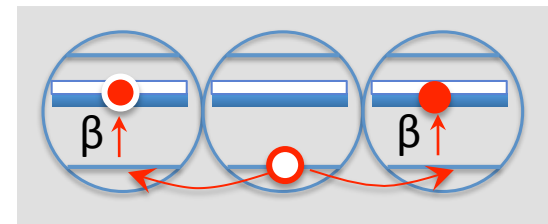
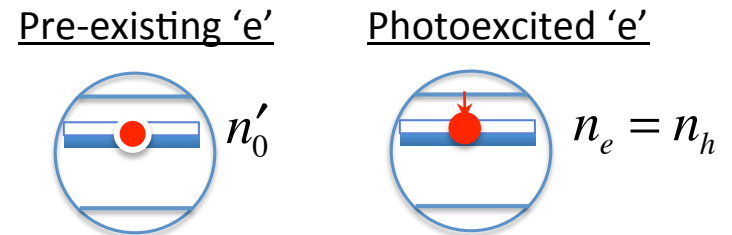
Recombination Controlled by the Electron Occupancy of the Intragap Band

Ethanedithial (EDT) treatment



A. Fidler, J. Gao, V.I. Klimov,
Nature Phys. March, 2017

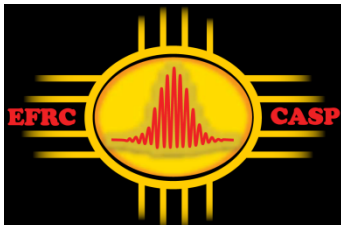
Mixed-states photoconductance



P. Nagpal & V.I. Klimov, *Nature Comm.* 2, (2011)

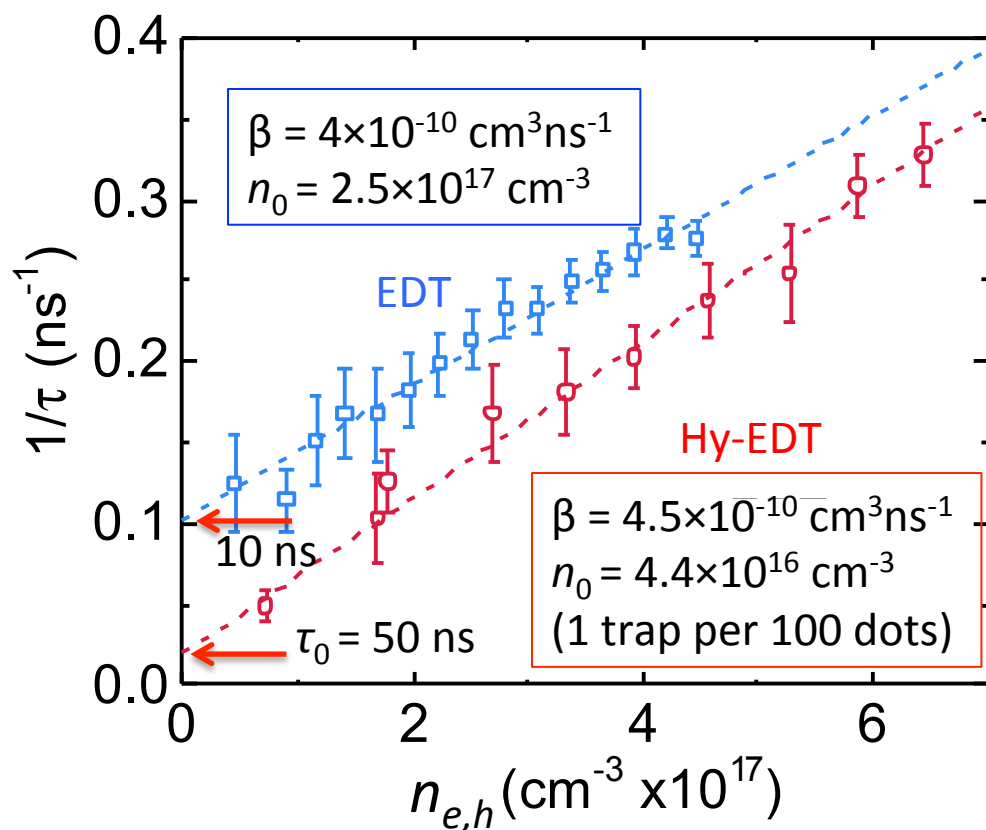
$$\frac{dn_h}{dt} = -\beta n_h (n'_0 + n_h)$$

$$\frac{1}{\tau_{eh}} = \beta (n'_0 + n_h) = \frac{1}{\tau_0} + \beta n_h; \quad \frac{1}{\tau_0} = \beta n'_0$$



Effect of Surface Treatment on Recombination Parameters

■ EDT + Hydrazine (Hy) treatment



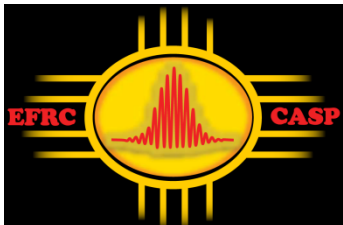
$$n'_{0,HY+EDT} < n'_{0,EDT}$$

Treatment with hydrazine:

- Does not change the nature of the intra-gap band
- Reduces its electron occupancy (reduces the level of doping by a factor of ~6)

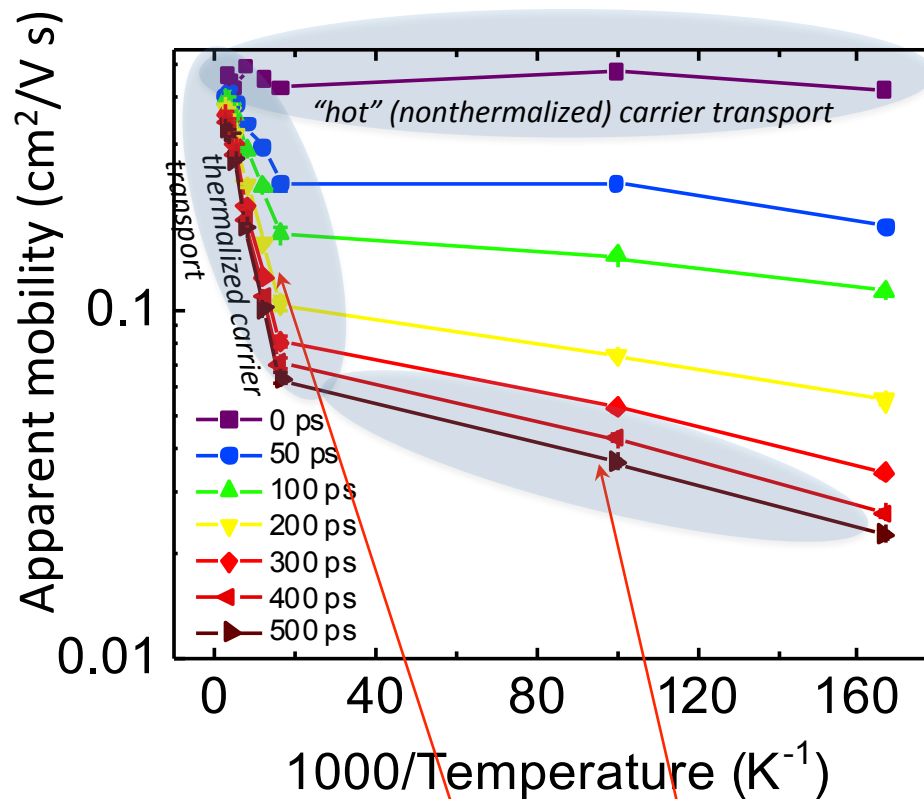
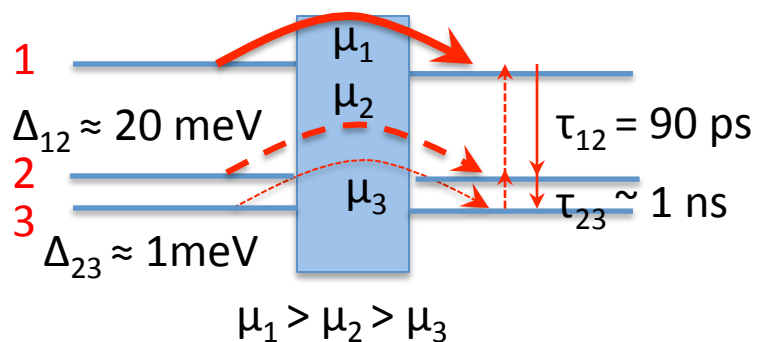
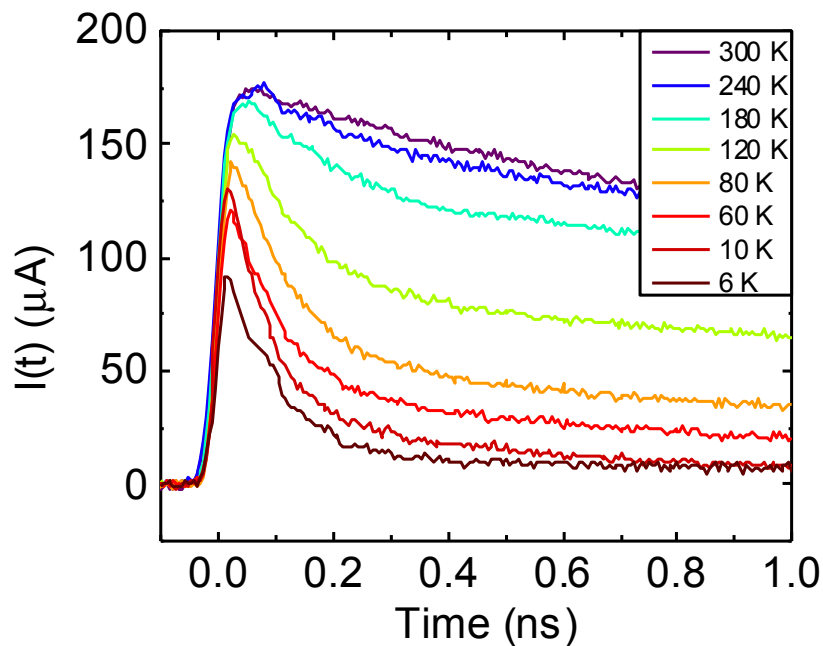
These measurements yield:

- Dopant concentration
- Coefficient of hole capture by intra-gap states/band

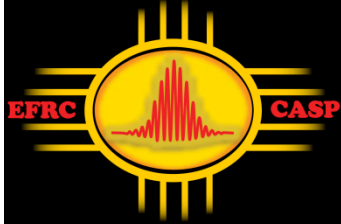


“Hot” vs. Thermalized Carrier Transport: Involvement of Three Intrinsic QD states?

■ Early time photocurrent dynamics ($t < 1$ ns)



$$\mu = \frac{\mu_1 e^{-(\Delta_{12} + \Delta_{23})/kT} + \mu_2 e^{-\Delta_{23}/kT} + \mu_3}{1 + e^{-\Delta_{12}/kT} + e^{-(\Delta_{12} + \Delta_{23})/kT}}$$



Fine Structure of Exciton States in PbSe QDs: Electron-Hole Exchange Interaction

PRL 105, 067403 (2010)

PHYSICAL REVIEW LETTERS

week ending
6 AUGUST 2010

PHYSICAL REVIEW B 82, 245303 (2010)

Revealing the Exciton Fine Structure of PbSe Nanocrystal Quantum Dots Using Optical Spectroscopy in High Magnetic Fields

R. D. Schaller,¹ S. A. Crooker,² D. A. Bussian,¹ J. M. Pietryga,¹ J. Joo,¹ and V. I. Klimov¹

¹Chemistry Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

²National High Magnetic Field Laboratory, Los Alamos, New Mexico 87545, USA

(Received 7 April 2010; published 4 August 2010)

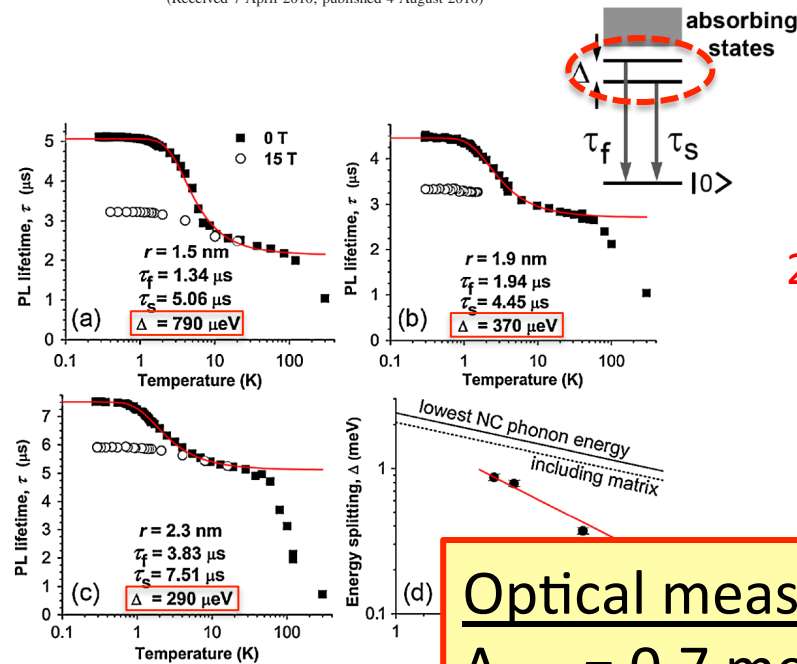


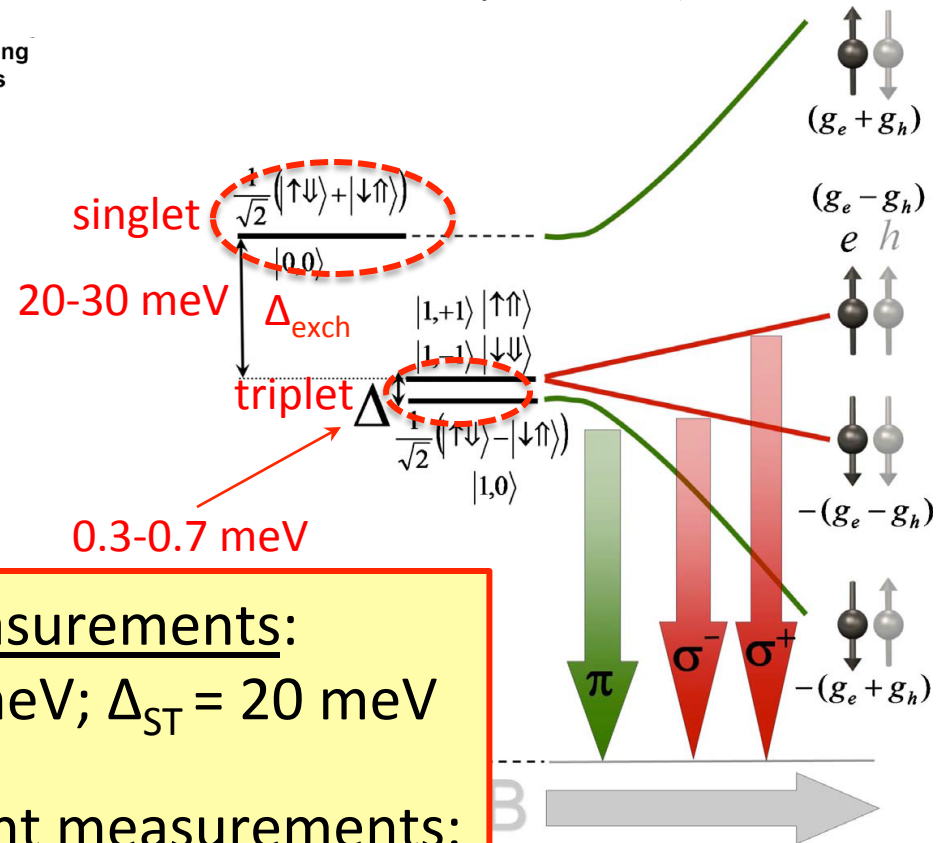
FIG. 2 (color online). (a)–(c) τ vs T for $B = 0$ T (black points). Lines are fits to $\tau(T)$ (see text). Open symbols show $\tau(T)$ at $B = 15$ T. (d) The energy splitting between the two lowest exciton levels versus NC radius.

Band-edge excitons in PbSe nanocrystals and nanorods

J. G. Tischler, T. A. Kennedy, E. R. Glaser, Al. L. Efros, E. E. Foos, J. E. Boercker, T. J. Zega, R. M. Stroud, and S. C. Erwin

Naval Research Laboratory, Washington, DC 20375, USA

(Received 1 October 2010; published 6 December 2010)

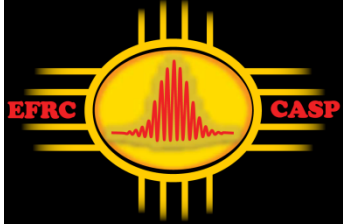


Optical measurements:

$$\Delta_{T1,2} = 0.7 \text{ meV}; \Delta_{ST} = 20 \text{ meV}$$

Photocurrent measurements:

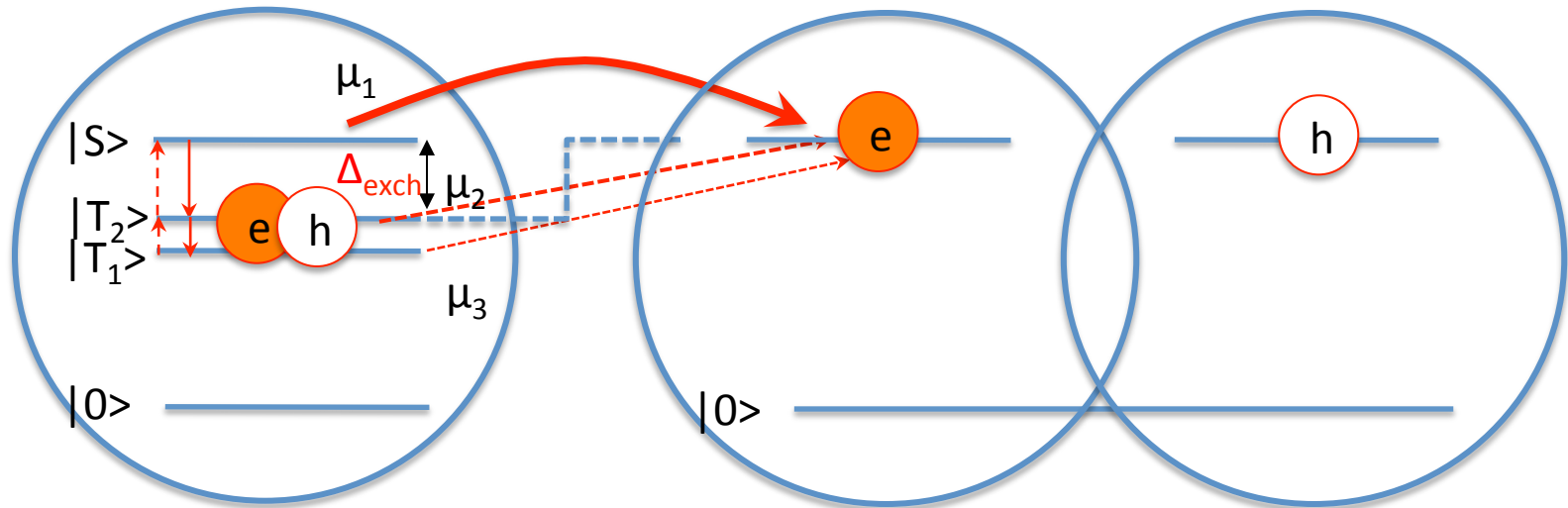
$$\Delta_{T1,2} = 0.8 \text{ meV}; \Delta_{ST} = 20 \text{ meV}$$



Effects of e-h Exchange Interactions in Early Time Photoconductance Dynamics: “e-h Exchange Blockade”

Initial (photoexcited) state

Charge-separated state

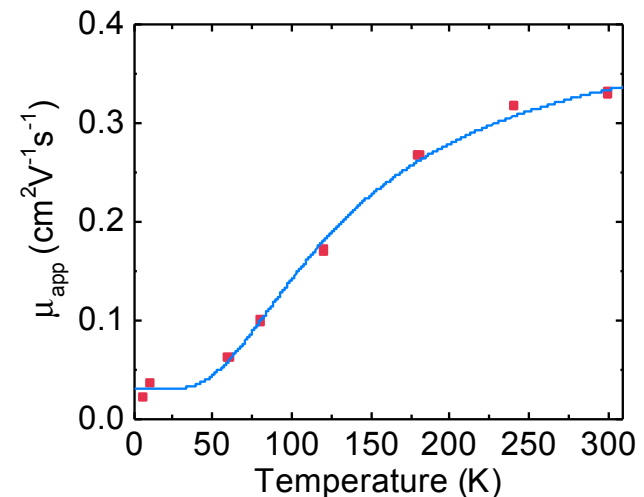


STRONG e-h EXCHANGE

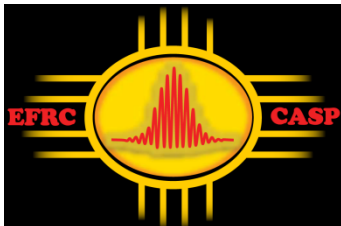
NO e-h EXCHANGE

$$\mu = \frac{\mu_1 e^{-(\Delta_{12} + \Delta_{23})/kT} + \mu_2 e^{-\Delta_{23}/kT} + \mu_3}{1 + e^{-\Delta_{12}/kT} + e^{-(\Delta_{12} + \Delta_{23})/kT}}$$

Observed only at the initial charge-separation step!



A. Fidler, J. Gao, V.I. Klimov,
Nature Phys. March, 2017



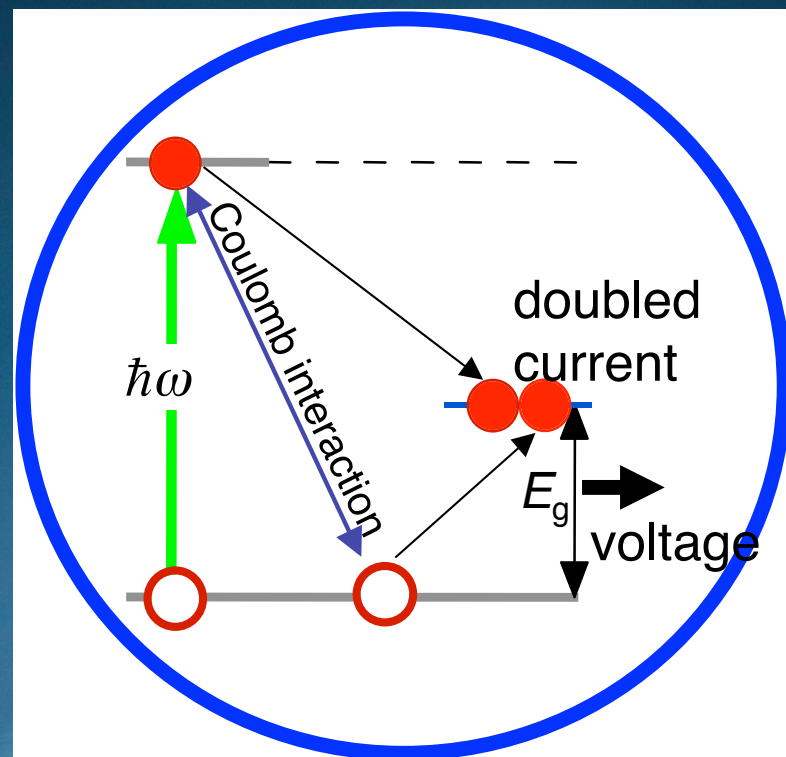
Carrier Multiplication: *Two for the Price of One*

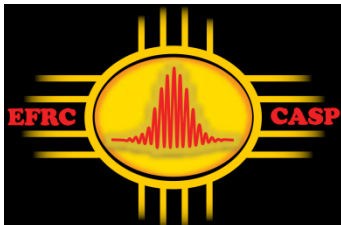
Make solar cells as small as a molecule, and you get more than you bargained for. Could this be the route to limitless clean power, asks Herb Brody

New Scientist

May 27, 2006

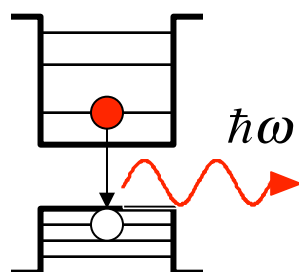
Two
for the
price of one





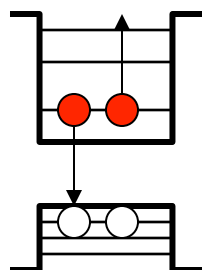
Ultrafast Auger Recombination of Biexcitons: A Blessing and a Curse

■ Single excitons: slow radiative decay



PbSe NCs
 $\tau_x \approx 1000$ ns

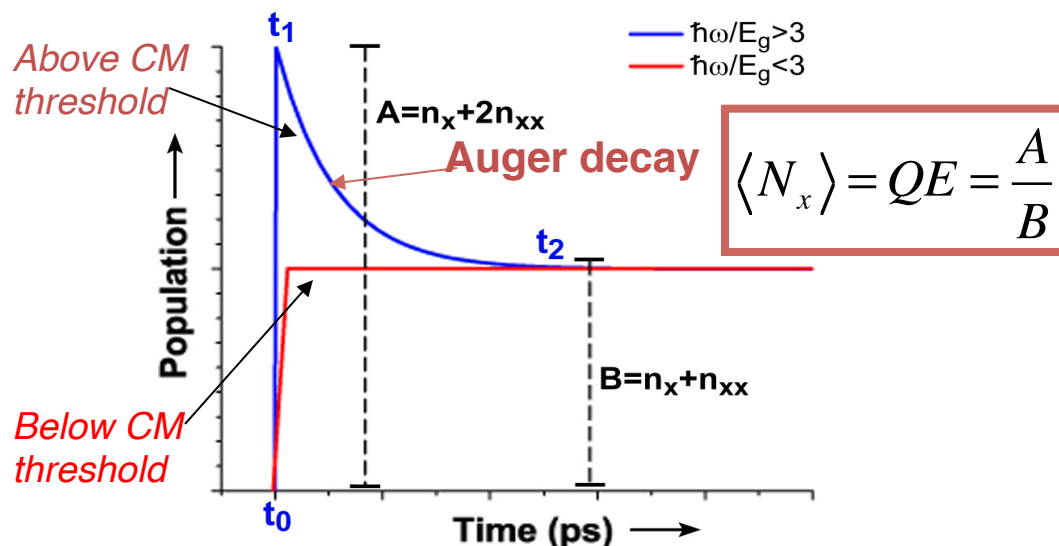
■ Multi-excitons: Fast nonradiative Auger decay



PbSe NCs
 $\tau_{xx} < 0.1$ ns

V. Klimov *et al.*,
Science **287**, 1011
(2000)

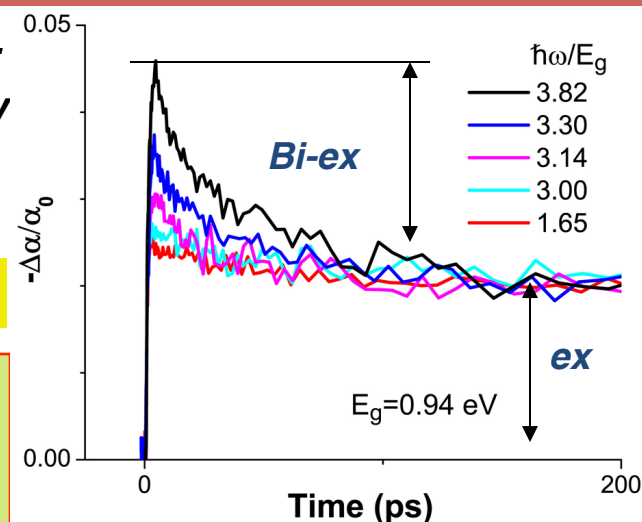
➤ Dynamical method for measuring CM efficiency

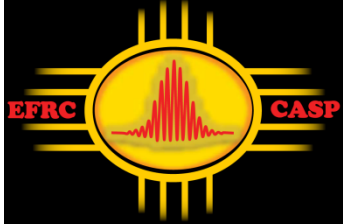


➤ Experiment: Photon energy scanned

$QE_{\max} = 220\%$

R. D. Schaller and
V. I. Klimov, *Phys.*
Rev. Lett. **92**,
186601 (2004)

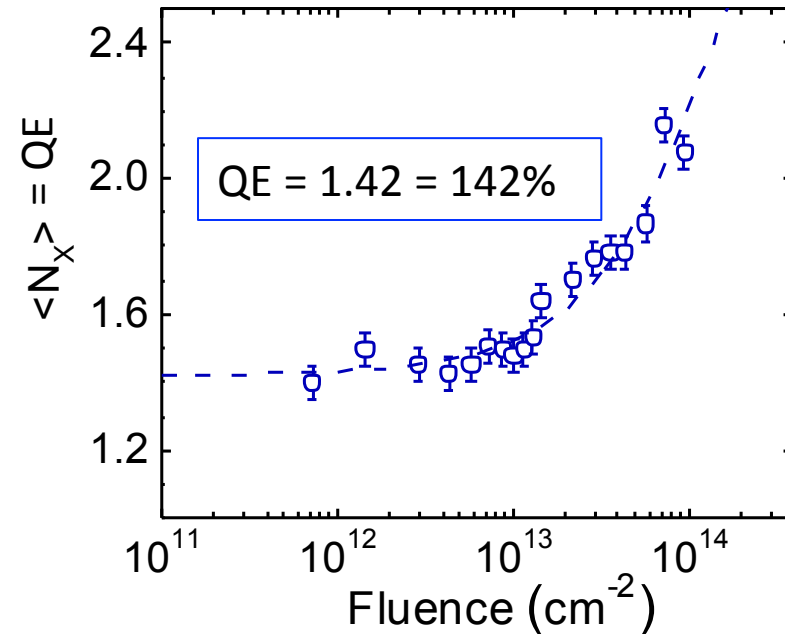
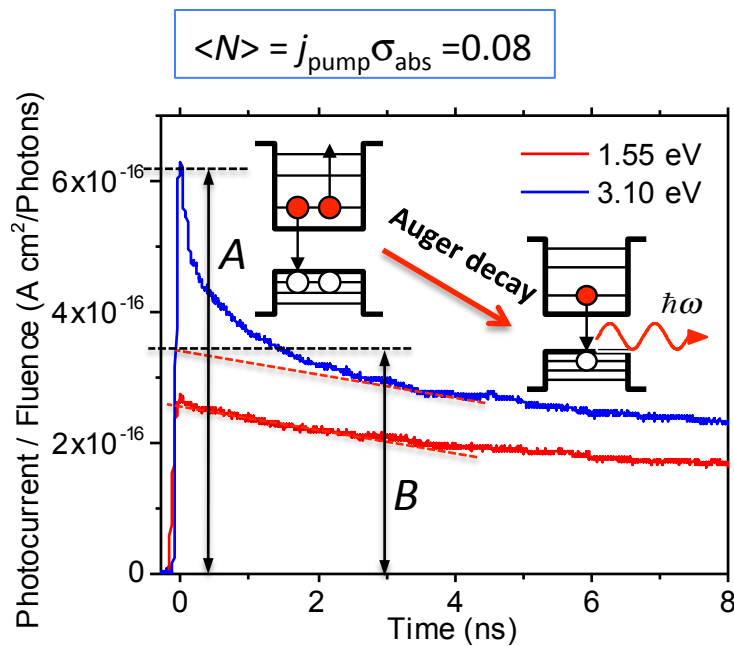




CM in Films of Coupled PbSe QDs via Transient Photocurrent

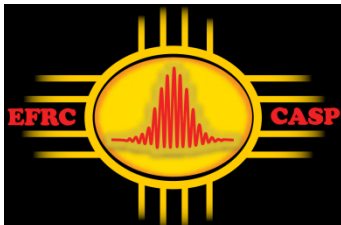
■ CM signature in TPC: 1.5 eV vs. 3.0 eV excitation

$$E_g = 0.69 \text{ eV}; \text{ CM threshold} = 2.85E_g = 2.0 \text{ eV}$$



$\langle N_x \rangle$ - number of excitons per photoexcited QD
 $\langle N_x \rangle = A/B$
 $QE = \lim_{\text{fluence} \rightarrow 0} \langle N_x \rangle = 1.42$

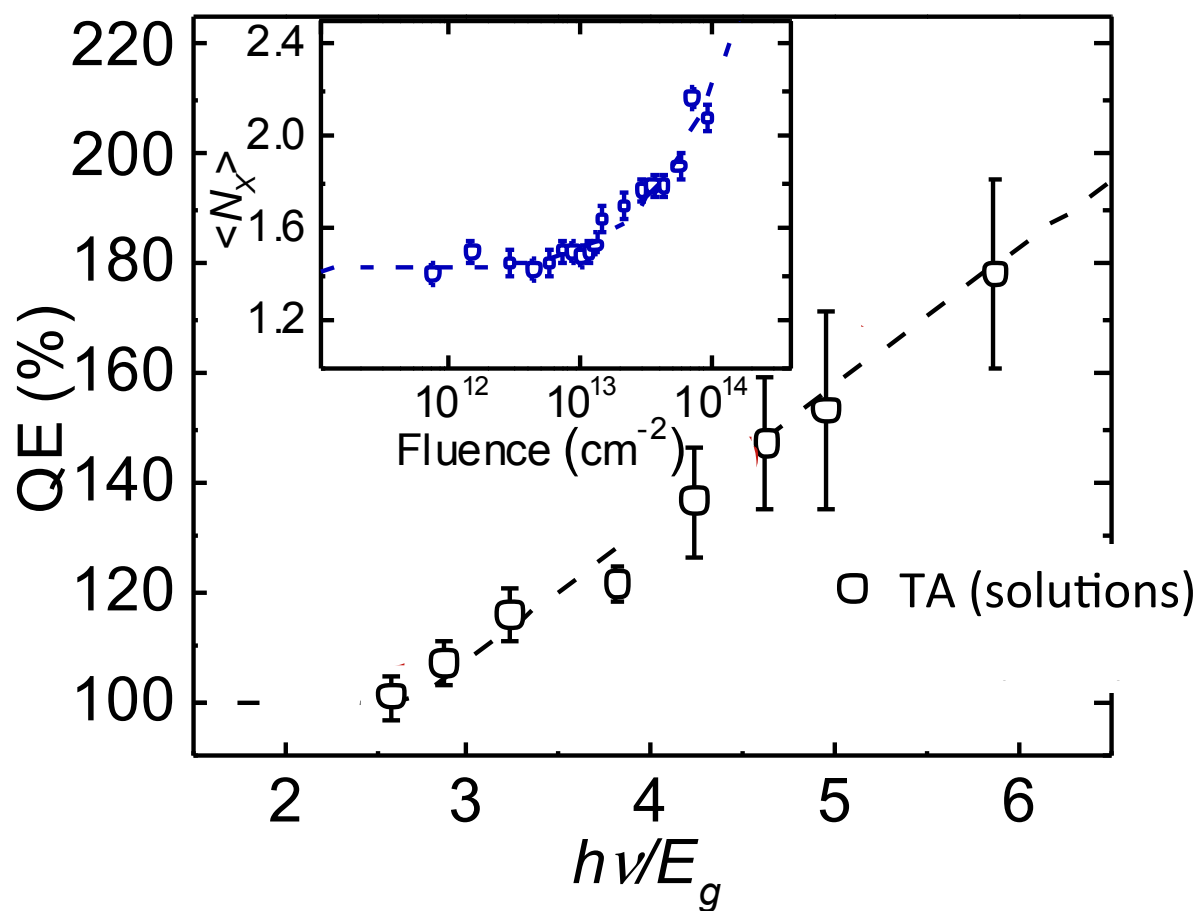
average exciton multiplicity:
 QE of photon-to-exciton conversion



CM in QD Solutions (TA) vs. Films of Coupled QDs (TPC)

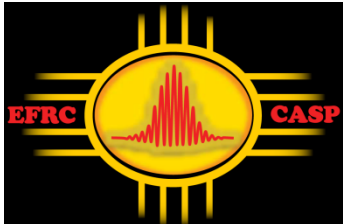
■ CM in PbSe QDs: Solutions vs. films (EDT treatment; $T = 300$ K)

$h\nu = 1.5$ & 3 eV; $E_g = 0.5$ to 0.75 eV

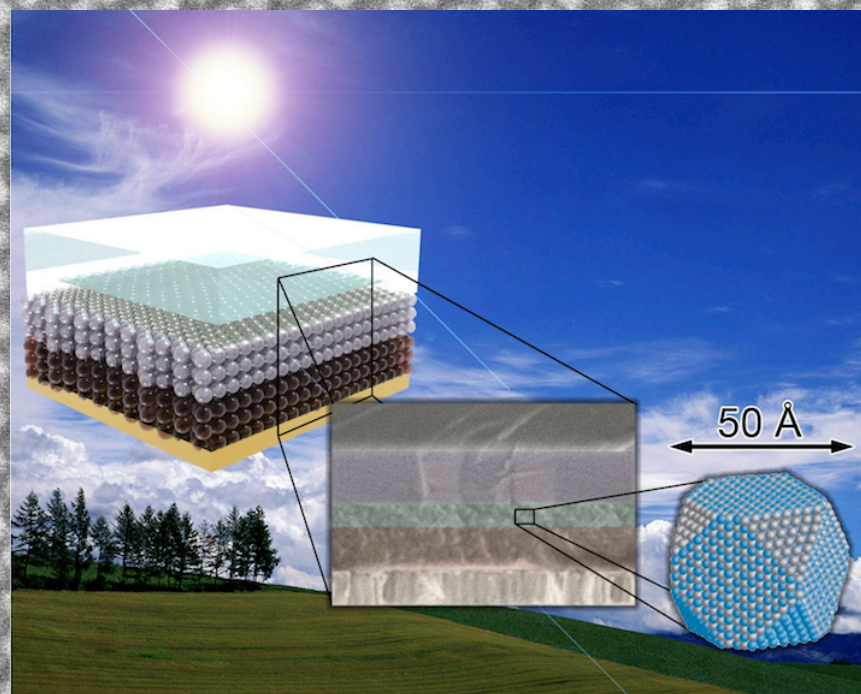
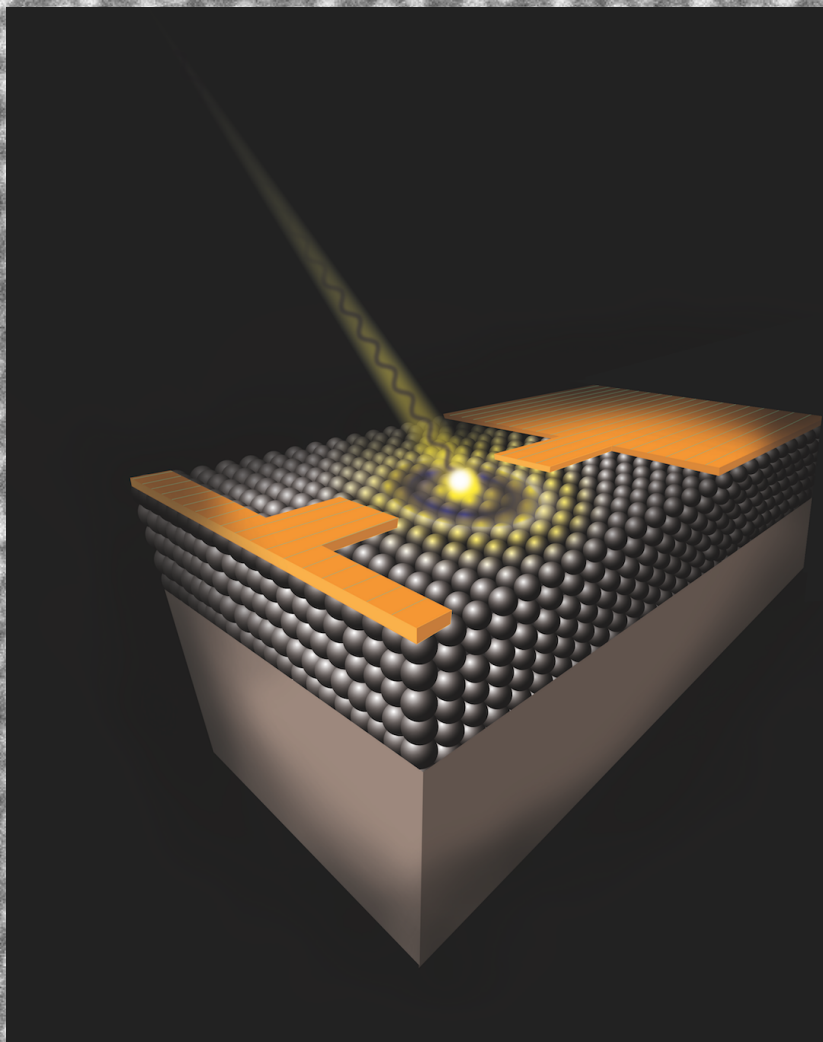


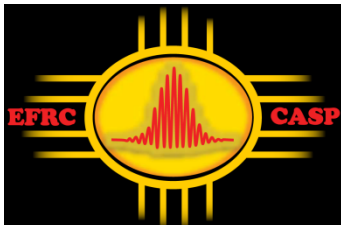
QD solutions: L. Padilha, et al., *Acc. Chem. Res.* **46**, 1261 (2013)
J. Stewart, et al., *J. Phys. Chem. Lett.* **4**, 2061 (2013)

QD films: J. Gao, A. Fidler, V. Klimov, *Nature Comm.* (Sep. 8, 2015)



TPC Spectroscopy: New Insights into Physics of Charge Transport and Operation of Practical Devices



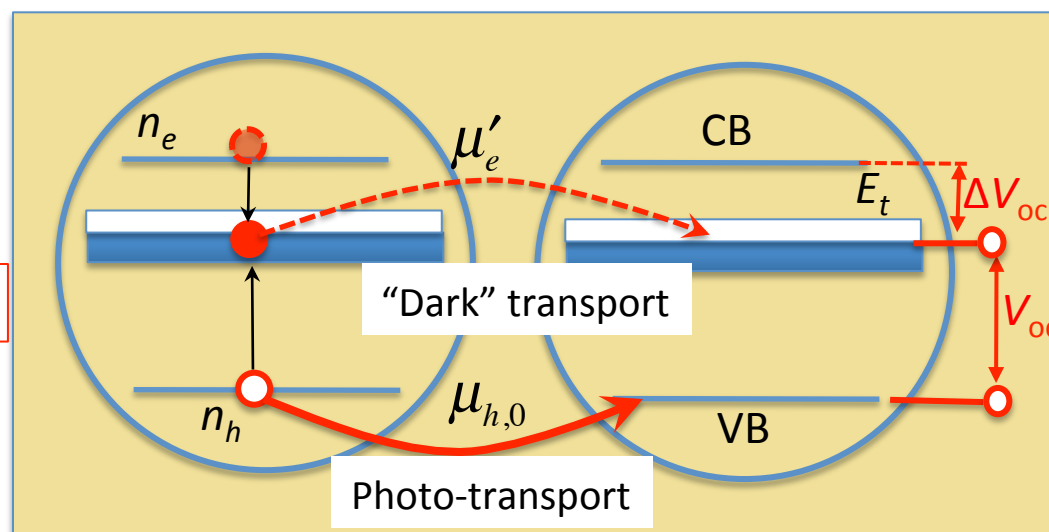


Summary: Charge Transport and Recombination in QD solids

$$\mu_{0,h} = (0.2 - 1) \text{ cm}^2 / \text{Vs}$$

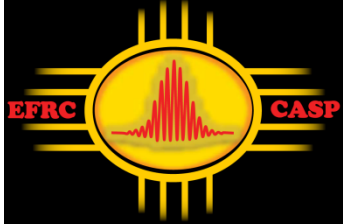
$$\tau_{e,t} = 0.5 - 1 \text{ ns}$$

$$\tau_{eh} = 10 - 100 \text{ ns}$$



J. Gao, A. Fidler, V. I. Klimov, *Nature Comm.* **6**, 8185 (2015)
A. Fidler, J. Gao, V.I. Klimov, *Nature Phys.* March (2017)

- **Early time photoconductance is T-insensitive suggesting tunneling mechanism**
 - Intrinsic mobilities of band-edge states of $\sim 1 \text{ cm}^2/\text{Vs}$
- **V_{oc} deficit due fast, sub-ns electron trapping ($\sim 50\%$ loss of photocurrent)**
 - Characteristic timescale: $\tau_{e,t} = 0.5 - 1 \text{ ns}$
- **Memory-less non-geminate recombination with lifetimes limited by “dark” occupancy of the intra-gap band**
 - Characteristic timescale: $\tau_{eh} = 10 - 100 \text{ ns}$



Nanotechnology and Advanced Spectroscopy Team

Los Alamos, 2014

